

CLAIMS

1. Glass plate intended to constitute a plate-shaped product provided on at least part of at least one  
5 of its faces with a metal coating, the said plate being resistant to coloration due to at least one metal species  $M^{n+}$  of the said metal coating, which species, under the conditions in which the product is manufactured and/or used, would be liable to  
10 migrate into the glass from its surface and then undergo reduction to the species  $M^0$  responsible for the coloration, characterized in that it includes, at least on the surface and on at least one face sensitive to coloration, a composition capable of  
15 limiting or preventing the said migration and/or the said reduction of the one or more  $M^{n+}$  species.
2. Plate according to Claim 1, characterized in that  
20 it is produced so as to present, on the surface and on the face or faces sensitive to coloration and at least over a depth to which the  $M^{n+}$  species is capable of migrating, a quantity of reducing agent capable of reducing the  $M^{n+}$  species, this quantity being at most equal to  $1.40 \times 10^{-7}$  mol/cm<sup>2</sup>  
25 when the  $M^{n+}$  metal species is  $Ag^+$ .
3. Plate according to Claim 2, characterized in that  
30 the reducing agent is chosen from elements having several oxidation states, such as Fe, S, Sn, Sb and mixtures of these elements.
4. Plate according to either of Claims 2 and 3,  
35 characterized in that the said quantity of reducing agent is at most equal to  $7 \times 10^{-8}$  mol/cm<sup>2</sup>, especially at most equal to  $3.5 \times 10^{-8}$  mol/cm<sup>2</sup>.
5. Plate according to one of Claims 1 to 4,  
characterized in that it is provided, on the

- coloration-sensitive face or faces, with a layer acting as a barrier to the migration of the  $M^{n+}$  species, to which barrier layer continuous or discontinuous functional layers are capable of adhering, and which barrier layer is unable to react chemically with the said functional layers so as to degrade the properties thereof.
- 5
6. Plate according to Claim 5, characterized in that
- 10 the barrier layer is chosen from layers based on one or more metal oxides, such as  $SiO_xC_y$  ( $x = 0-2$ ;  $y = 0-1$ , the limits being excluded),  $MgO$ ,  $ZnO$  and  $Sn_xZn_yO_z$  ( $x$  and  $y$  each having a non-zero value;  $z = 2x + y$ ), and the layers based on  $AlN$  and
- 15  $Si_3N_4/AlN$  mixtures.
7. Plate according to Claim 5, characterized in that the layer is non-conducting.
- 20 8. Plate according to one of Claims 1 to 7, characterized in that the alkaline-earth metal content includes barium only in a limited proportion, the  $BaO$  content not exceeding 2% by weight of the glass composition.
- 25
9. Plate according to one of Claims 1 to 8, characterized in that it has an alkali metal content under conditions that ensure what is called a "mixed-alkali" effect.
- 30
10. Plate according to Claim 9, characterized in that the alkali metals are lithium, sodium and potassium.
- 35 11. Plate according to Claim 10, characterized in that the alkali metals are sodium and potassium that are present in the form of their corresponding oxides,  $Na_2O$  and  $K_2O$ , in molar quantities that satisfy the following relationship:

$$0.35 \leq K_2O / K_2O + Na_2O \leq 0.65.$$

12. Plate according to one of Claims 1 to 11,  
5 characterized in that it has an alumina weight  
content not exceeding 3%.
13. Plate according to one of Claims 1 to 12,  
10 characterized in that it has a silica weight  
content not exceeding 65%.
14. Plate according to one of Claims 1 to 7,  
15 characterized in that a surface layer capable of  
limiting or preventing the migration or reduction  
of the one or more  $M^{n+}$  species has a thickness of  
less than 100  $\mu m$ , preferably less than 50  $\mu m$  and  
especially less than 20  $\mu m$ .
15. Plate according to one of Claims 1 to 14,  
20 characterized in that it is produced in the form  
of a ribbon obtained by the float process on a  
bath of molten metal, such as a bath of tin, that  
coloration-sensitive face of the glass in the  
finished product being the one on the opposite  
25 side to that which was in contact with the tin at  
least in the case of a glass as defined in one of  
Claims 2 to 4.
16. Plate according to one of Claims 1 to 15,  
30 characterized in that it has a strain-point  
temperature above 550°C.
17. Plate according to either of Claims 15 and 16, the  
35 said plate being produced on a bath of molten tin,  
characterized in that its composition is chosen so  
as to allow it to be produced under conditions  
that discourage the migration of  $Sn^{2+}$  or  $H_2$  into  
the atmosphere face of the glass ribbon, the  $H_2$   
content of the  $N_2+H_2$  reducing atmosphere above the  
bath being lowered relative to the normal working

- 5 conditions, in order to decrease the SnS saturation vapour pressure and the temperature of the bath and that of the glass being lowered relative to the normal working conditions, the sulphate content of the glass being advantageously lowered relative to the normal working conditions in order to reduce the SnS content.
- 10 18. Plate according to Claim 17, characterized in that at least one of the following conditions is satisfied:
- viscosity of the glass corresponding to  $\log \eta = 3.5$ , at a temperature not exceeding  $1230^{\circ}\text{C}$ , preferably between  $1180$  and  $1220^{\circ}\text{C}$ ;
  - 15 - temperature of the bath not exceeding  $1220^{\circ}\text{C}$ ;
  - temperature at which the glass is poured onto the bath of molten tin not exceeding  $1280^{\circ}\text{C}$ ;
  - $\text{H}_2$  content in the atmosphere of the bath 7% by volume or less.
- 20 19. Plate according to one of Claims 1 to 18, characterized in that it contains at least one element capable of colouring the glass with a colour that is complementary to the colour at risk
- 25 owing to the diffusion of  $\text{M}^{n+}$ , for example  $\text{Co}^{2+}$ .
20. Plate according to Claim 1, having the following composition, the proportions by weight of the constituents being the following:
- |    |                         |   |        |
|----|-------------------------|---|--------|
| 30 | $\text{SiO}_2$          | : | 65-75% |
|    | $\text{Al}_2\text{O}_3$ | : | 0-3%   |
|    | $\text{ZrO}_2$          | : | 2-7%   |
|    | $\text{Na}_2\text{O}$   | : | 0-8%   |
|    | $\text{K}_2\text{O}$    | : | 2-10%  |
| 35 | $\text{CaO}$            | : | 3-10%  |
|    | $\text{MgO}$            | : | 0-5%   |
|    | $\text{SrO}$            | : | 3-12%  |
|    | $\text{BaO}$            | : | 0-2%   |
|    | Other oxides            | : | 0-2%.  |

21. Process for manufacturing a coloration-resistant glass plate, as defined in one of Claims 1 to 20, in a float process in which it floats on a bath of molten tin, characterized in that the float process is carried out under the following conditions:
- viscosity of the glass corresponding to  $\log \eta = 3.5$ , at a temperature not exceeding  $1230^{\circ}\text{C}$ , preferably between  $1180$  and  $1220^{\circ}\text{C}$ ;
  - temperature of the bath not exceeding  $1220^{\circ}\text{C}$ ;
  - temperature at which the glass is poured onto the bath of molten tin not exceeding  $1280^{\circ}\text{C}$ ;
  - $\text{H}_2$  content in the atmosphere of the bath 7% by volume or less.
22. Application of the glass plate as defined in one of Claims 1 to 20, or obtained by the process as defined in Claim 21, to the manufacture of plate-shaped glass products that have received metal coatings liable to generate a coloration during treatments, especially at high temperature, during their manufacture and/or during use, owing to interactions between the components of the glass itself and these metals, in particular to the manufacture of emissive displays, such as plasma display panels, electroluminescent screens and field-emission displays, flat lamps, index-graded microlenses and rear windows for motor vehicles.